# DEVELOPMENT OF AN ENAMEL ON A EUTECTIC BASIS

---

DISSERTATION

PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

---

BY

HAROLD ELLIS SIMPSON, B.Cer.E., M.S.

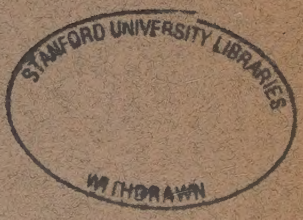
L. C.

---

The Ohio State University

1929

Published, 1930



3781
O37S

UNCLASSED

# DEVELOPMENT OF AN ENAMEL ON A EUTECTIC BASIS

---

DISSERTATION

PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

---

BY

HAROLD ELLIS SIMPSON, B.Cer.E., M.S.

---

The Ohio State University

1929

Published, 1930

## Preface

This investigation was undertaken with the object of developing a eutectic solvent for an enamel by the combination of several eutectics. Then by additions of silica or some other refractory, to harden the enamel or increase its refractoriness up to the limit of its capability to dissolve silica without endangering its bonds to the metal body. This naturally involved a study of the eutectic compositions of the $RO–B_2O_3–SiO_2$ systems. Since the $Na_2O–B_2O_3–SiO_2$ eutectic, the $K_2O–B_2O_3–SiO_2$ eutectic, and the $PbO–B_2O_3–SiO_2$ eutectics are known, a knowledge of the $CaO–B_2O_3–SiO_2$ system as to eutectic development was necessary. A study of the high $B_2O_3$ area of this system was made at approximately 4 per cent intervals. A member high in CaO and in $SiO_2$, and which on repeated fusions showed practically 100% glass, was selected as a practical member to blend with the $Na_2O–B_2O_3–SiO_2$ eutectic and the $PbO–B_2O_3–SiO_2$ eutectic to form an eutectic solvent for an enamel.

Combinations of these eutectics and the $CaO–B_2O_3–SiO_2$ mixtures were made and applied to cast iron by the dry process. Additions of $SiO_2$ were also made to these enamels up to 1.5 molecular equivalents. The physical properties of these enamels such as brilliancy, smoothness of surface, texture, bonding power, solubility in water, and resistance to acid attack were also determined.

## Table of Contents


Title page ..... i

Preface ..... ii

Table of Contents ..... iii

Introduction ..... 5

Preliminary Study ..... 5

Method of Study and Raw Materials ..... 7

Results ..... 8

Eutectics as an Enamel Basis ..... 12

Results of Dry-Process Cover-Coat Test on Black Ground Coat ..... 15

Results of Dry-Press Cover-Coat Test on Commercial Ground Coat ..... 16

Actions of Various Acids on Enamels ..... 16

Water Solubility ..... 19

Summary ..... 20

Acknowledgment ..... 22

Bibliography ..... 22

Autobiography ..... 23

# THE DEVELOPMENT OF AN ENAMEL ON A EUTECTIC BASIS[1]

By Harold Ellis Simpson

ABSTRACT

The object of the investigation was to develop a eutectic solvent for an enamel by the combination of several eutectics, then to add silica to increase the refractoriness of the enamel up to the limit of its capability to dissolve silica without endangering its bond to the metal body. This naturally involved a study of the eutectic compositions of the $RO–B_2O_3–SiO_2$ systems. Since the $Na_2O–B_2O_3–SiO_2$, $K_2O–B_2O_3–SiO_2$, and $PbO–B_2O_3–SiO_2$ deformation eutectics are known, a knowledge of the $CaO–B_2O_3–SiO_2$ system was necessary. A study of the high $B_2O_3$ area of this system was made at approximately 4% intervals. A member high in CaO and $SiO_2$, and which on repeated fusions showed practically 100% glass, was selected as a practical member to blend with the $Na_2O–B_2O_3–SiO_2$ and the $PbO–B_2O_3–SiO_2$ eutectic to form a eutectic solvent for an enamel.

Combinations of these eutectics and the $CaO–B_2O_3–SiO_2$ mixture were made and applied to cast iron by the dry process. Additions of $SiO_2$ were also made to these enamels up to 1.5 molecular equivalents. The physical properties of these enamels such as brilliancy, smoothness of surface, texture, bonding power, solubility in water, and resistance to acid attack were also determined.

## Introduction

A fundamental consideration in the development of an enamel is the eutectic solvent. If $RO–R_2O_3–SiO_2$ eutectics can be so combined as to dissolve the maximum amount of silica we would have an enamel with the greatest resistance to service abuse.

The term "eutectic" or "deformation eutectic"[2] is used here to designate that mixture which requires the least heat treatment to cause fluidity sufficient to result in the deformation of the mixture.

The object of this investigation was to develop a eutectic solvent and then by the addition of silica or some other refractory to harden the enamel or to increase its refractoriness up to the limit of its capability to dissolve silica without endangering its bond to the metal body.

A review of the literature shows that an enormous amount of work has been done on the thermochemical behavior of the chief constituents of an enamel.[3]

## Preliminary Study

The first stage of the study was the $CaO–B_2O_3–SiO_2$ system in the high $B_2O_3$ corner of the triaxial. To get around bloating due to the liberation of the chemically combined water of the boric acid, fusions were made of the various members and these fusions were used as end members. Trouble was encountered in making the fusions. The members high in lime of both

[1] Presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School, Ohio State University. Received June 10, 1929.

[2] See Bibliography, ref. 1 (at end of paper).

[3] See Bibliography, ref. 2 to 38.

the lime-borosilicates and lime-borates would eat through the walls and completely destroy the crucible.

Many types of crucibles were used, including fire clay, high bauxite, chemical porcelain, dense porcelain (cone 23), alundum (Norton Company), magnesia (Norton Company), sillimanite (Champion Spark Plug Company), fused silica, and graphite crucibles.

Fused silica was satisfactory for lime-borosilicates but not for lime-borates. A fusion was made in graphite crucibles of both lime-borosilicates and lime-borates, but there was a question as to whether the melt did not attack clay bond in the crucible.

To get away from this contamination of melts by the crucible, bars 1 by 1 by $4^3/_8$ inches were made of the end members. They were dry pressed, using water as a bond and a pressure of about one and one-half tons. These bars were placed on platinum-covered clay triangular supports, heated in a Hoskins resistance furnace until they sagged under their own weight, then turned over and heated until they sagged back again. These bars ground to pass a 100-mesh screen and made into cones, bloated as their fusion temperature was approached, especially those high in $B_2O_3$. The cones behaved little better than those made from the raw materials. This method was abandoned.

Melts were made of three lime-borosilicate members in fused silica crucibles. These melts were analyzed to determine any change in composition.

The following results were obtained from the analysis:

| Member 1 | Trials | | | | |
|---|---|---|---|---|---|
| Ingredient | (1) | (2) | | Mean | From diagram |
| $SiO_2$ | 33.66% | 33.60% | = | 33.63% | 34.2% |
| CaO | 4.34 | 4.42 | = | 4.38 | 3.6 |
| $B_2O_3$ (by difference) | 62.00 | 61.98 | = | 61.99 | 62.2 |
| | 100.00 | 100.00 | | 100.00 | 100.0 |

| Member 21 | Trials | | | | |
|---|---|---|---|---|---|
| Ingredient | (1) | (2) | | Mean | From diagram |
| $SiO_2$ | 13.68% | 13.10% | = | 13.39% | 14.8% |
| CaO | 3.94 | 3.86 | = | 3.90 | 3.5 |
| $B_2O_3$ (by difference) | 82.38 | 83.04 | = | 82.71 | 81.7 |
| | 100.00 | 100.00 | | 100.00 | 100.0 |

| Member 16 | Trials | | | | |
|---|---|---|---|---|---|
| Ingredient | (1) | (2) | | Mean | From diagram |
| $SiO_2$ | 17.80% | 17.48% | = | 17.64% | 15.4% |
| CaO | 22.88 | 22.68 | = | 22.78 | 21.5 |
| $B_2O_3$ (by difference) | 59.32 | 59.84 | = | 59.58 | 63.1 |
| | 100.00 | 100.00 | | 100.00 | 100.0 |

Member 16 was fused twice owing to a white opaque scum that formed on top of a clear glass. The fusion was ground to pass a 100-mesh sieve and fused a second time in a silica crucible. A small amount of scum appeared.

This double fusion may account for the greater variation between "mean" and "diagram" results in this member than was noted in the others.

It is believed that these analyses were well within the accuracy of the other measurements possible in this experiment, including weighing up of the various members, temperature measurements, etc.

The white milky scum on top of member 16 was examined (just after cooling from fusion) under the microscope by Professor McCaughey. The scum appeared to be well vitrified and apparently had very little that was not in solution. It had an index of $< 1.46$. On examination about one-half hour later it showed distinct evidence of devitrification and crystallization. This delayed crystallization is a characteristic of borosilicate glasses. We, therefore, had the added problem of getting all the material into solution. The glass below (clear) had an index of about 1.57.

Considerable difficulty was encountered in finding a binder for these glasses in making up cones. No aqueous solution could be used because glasses or fusions took up water quite readily and on fusion liberated this chemically-combined water, bloating the cones so that a true deformation could not be obtained. Many different binders were used, such as collodion, xylene, benzol, saturated alcoholic solution of balsam, and amyl acetate or banana oil.

Collodion was unsatisfactory as it would not mix with material and the ether would evaporate before cones could be made.

Xylene and benzol alone were unsatisfactory as they would not give cones proper strength in dry state for handling.

A saturated alcoholic solution of balsam and banana oil gave the best results, giving a cone that could be handled in dry state, would not bloat on fusion or leave any evidence of black coring or unfired organic matter in a deformed cone.

## Method of Study and Raw Materials

The method of procedure was to make up 200-g. batch end members. These members were made into bars about one inch square and four inches long, and were dry pressed. Water was used as a lubricant. After the bars were dried they were cut into cubes, 1 by 1 by 1 inch. The object in forming cubes was to have a material in such condition that it could be added to the crucible while the crucible was still in the furnace, and thus make successive fusions. The crucibles were too small for a 200-g. batch, hence the fusion of the batch was accomplished by fusing a few cubes at a time, bringing them to quiet fusion and pouring into a cast-iron ingot mold. The operation was repeated until the entire batch was fused. The materials thus accumulated were finally ground together into a single batch.

The raw materials used were Baker's C.P. crystalline boric acid and calcium carbonate. The flint used had the following analysis:

| | | | |
|---|---|---|---|
| $SiO_2$ | 99.42% | $TiO_2$ | 0.006 |
| Ignition loss | 0.09 | CaO | .02 |
| $H_2O$ | .03 | MgO | .01 |
| $Al_2O_3$ | .06 | KNaO | .14 |
| $Fe_2O_3$ | .04 | | |
| | | | 99.816% |

These end members were then ground to pass a 150-mesh screen, placed in ground glass stoppered bottles, and the bottles kept in a desiccator. The melts were first broken up in a steel mortar, then a magnet worked through the material to remove iron. The completed grinding was done with an agate mortar. Each member was weighed up in 5-g. batches. Three cones were made of each member. All cones were made about two-thirds standard size and banana oil (amyl acetate) was used as a binder. In

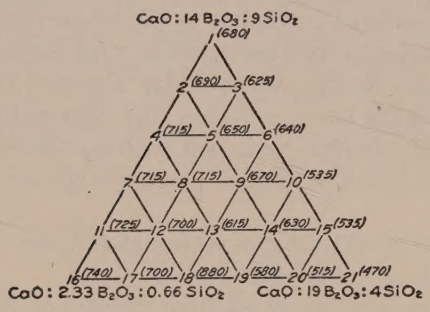



FIG. 1.

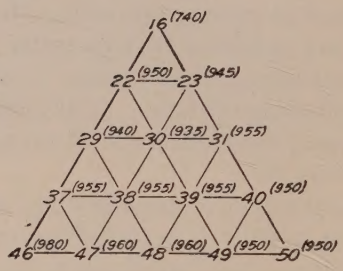



FIG. 2.

planting the cones in the plaque, finely-powdered alumina was used between cone and plaque to prevent reaction between the two.

The deformation behavior of the cones was watched from a peephole in the front door of an electrically-heated muffle furnace. Temperatures and time were recorded. The deformation was judged by the starting and finishing temperature and time. With time accurately taken, the interval between "started" and "down" is a measure of the comparative viscosities. For some of the cones high in $B_2O_3$, deformations were obtained before a temperature was raised sufficiently high to see into the furnace without the use of an electric light.

## Results[4]

**Study A** The first area studied was the area bound by members 1, 16, and 21. These end members have the following composition:

| Member | | | |
|---|---|---|---|
| 1 | CaO | $14B_2O_3$ | $9SiO_2$ |
| 16 | CaO | $2.33B_2O_3$ | $0.66SiO_2$ |
| 21 | CaO | $19B_2O_3$ | $4SiO_2$ |

[4] See Bibliography, reference 39.

These members were fused in a fused silica crucible and heated in a gas-fired surface combustion furnace. Member 16, on account of scum on top of the melt was fused twice.

TABLE I

End Members 1, 16, 21; 4% intervals

| Member | Temp. (°C) | Time "Started" | Time "Down" | Interval (min.) | Member | Temp. (°C) | Time "Started" | Time "Down" | Interval (min.) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 680 | 4:02 | 4:04 | 2 | 11 | 725 | 4:08 | 4:15 | 7 |
| 2 | 690 | 11:52 | 11:57 | 5 | 12 | 700 | 11:57 | 12:01 | 4 |
| 3 | 625 | 3:40 | 3:46 | 6 | 13 | 615 | 11:30 | 11:33 | 3 |
| 4 | 715 | 3:59 | 4:10 | 11 | 14 | 630 | 3:40 | 3:50 | 10 |
| 5 | 650 | 3:54 | 3:57 | 3 | 15 | 535 | 11:13 | 11:15 | 2 |
| 6 | 640 | 3:42 | 3:52 | 10 | 16 | 740 | 4:19 | 4:21 | 2 |
| 7 | 715 | 4:02 | 4:11 | 9 | 17 | 700 | | | |
| 8 | 715 | 4:03 | 4:10 | 7 | 18* | 880 | 12:00 | 12:54 | 54 |
| 9 | 670 | 3:57 | 4:00 | 3 | 19 | 580 | 11:20 | 11:24 | 4 |
| 10 | 535 | 1:12 | 1:15 | 3 | 20 | 515 | 11:07 | 11:11 | 4 |
| | | | | | 21 | 470 | 11:25 | 11:31 | 6 |

* Cone froze.

TABLE II

ARRANGED IN ORDER OF TEMPERATURE DEFORMATIONS

| Member | Temp. (°C) | Interval (min.) | Member | Temp. (°C) | Interval (min.) |
|---|---|---|---|---|---|
| 21 | 470 | 6 | 1 | 680 | 2 |
| 20 | 515 | 4 | 2 | 690 | 5 |
| 10 | 535 | 3 | 12 | 700 | 4 |
| 15 | 535 | 2 | 17 | 700 | |
| 19 | 580 | 4 | 8 | 715 | 7 |
| 13 | 615 | 3 | 7 | 715 | 9 |
| 3 | 625 | 6 | 4 | 715 | 11 |
| 14 | 630 | 10 | 11 | 725 | 7 |
| 6 | 640 | 10 | 16 | 740 | 2 |
| 5 | 650 | 3 | 18 | 880 | 54 |
| 9 | 670 | 3 | | | |

This series showed no relation between temperature of deformation and viscosities.

**Study B** The second area studied was bound by members 16, 46, and 50. These members have the following compositions:

| Member | | | |
|---|---|---|---|
| 16 | CaO | $2.33B_2O_3$ | $0.66SiO_2$ |
| 46 | CaO | $1.4B_2O_3$ | |
| 50 | CaO | $3.0B_2O_3$ | |

Members 46 and 50 were fused in a large platinum dish placed on a platinum tripod in an electric muffle furnace (Hoskins furnace). Member 50 having a scum on top of clear glass was fused twice. Member 46 came out a white opaque glass with the first fusion and was only fused once. Both fusions were held at about 1000°C for approximately three hours.

TABLE III

End Members 16, 46, 50; 4% intervals

| Member | Temp. (°C) | Time "Started" | Time "Down" | Interval (min.) |
|---|---|---|---|---|
| 22 | 950 | 4:48 | 4:49 | 1 |
| 23 | 945 | 4:44 | 4:48 | 4 |
| 29 | 940 | 4:43 | 4:47 | 4 |
| 30 | 935 | 4:43 | 4:46 | 3 |
| 31 | 955 | 4:49 | 4:50 | 1 |
| 37 | 955 | 4:49 | 4:50 | 1 |
| 38 | 955 | Very fast from 20–30 sec. | | |
| 39 | 955 | " " " " " | | |
| 40 | 950 | " " " " " | | |
| 46 | 980 | 4:59 | 5:01 | 2 |
| 47 | 960 | Very fast from 20–30 sec. | | |
| 48 | 960 | " " " " " | | |
| 49 | 950 | " " " " " | | |
| 50 | 950 | " " " " " | | |

TABLE IV

ARRANGED IN ORDER OF TEMPERATURE DEFORMATIONS

| Member | Temp. (°C) | Interval (min.) | Member | Temp. (°C) | Interval (min.) |
|---|---|---|---|---|---|
| 30 | 935 | 3 | 31 | 955 | 1 |
| 29 | 940 | 4 | 37 | 955 | 1 |
| 23 | 945 | 4 | 38 | 955 | Very fast |
| 22 | 950 | 1 | 39 | 955 | " " |
| 40 | 950 | Very fast | 47 | 960 | " " |
| 49 | 950 | " " | 48 | 960 | " " |
| 50 | 950 | " " | 46 | 980 | 2 |

This series showed no relation between deformation and viscosity.

**Study C** The third area studied was bound by members 21, 51, and 55. These members have the following composition:

| Member | | | |
|---|---|---|---|
| 21 | CaO | $19B_2O_3$ | $4SiO_2$ |
| 51 | CaO | $3.8B_2O_3$ | |
| 55 | CaO | $23B_2O_3$ | |

Glasses were made of each of the above end members (21 having been fused before in a fused silica crucible). Glasses 51 and 55 when poured

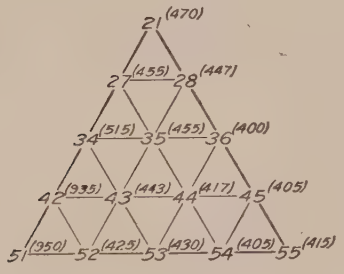



FIG. 3.

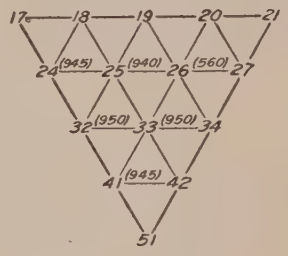



FIG. 4.

were white opaque glasses but on cooling an opaque scum crystallized on top; 51 and 55, however, were only fused once.

TABLE V

End Members 21, 51, 55; 4% Intervals

| Member | Temp. (°C) | Time "Started" | Time "Down" | Interval (min.) | Member | Temp. (°C) | Time "Started" | Time "Down" | Interval (min.) |
|---|---|---|---|---|---|---|---|---|---|
| 21 | 470 | 11:25 | 11:31 | 6 | 44 | 417 | 11:16 | 11:19 | 3 |
| 27 | 455 | 11:22 | 11:27 | 5 | 45 | 405 | 11:14 | 11:16 | 2 |
| 28 | 447 | 11:20 | 11:25 | 5 | 51 | 950 | | | |
| 34 | 515 | 11:40 | 11:43 | 3 | 52 | 425 | 11:18 | 11:20 | 2 |
| 35 | 455 | 11:23 | 11:27 | 4 | 53 | 430 | 11:18 | 11:22 | 4 |
| 36 | 400 | 11:13 | 11:15 | 2 | 54 | 405 | 11:13 | 11:16 | 3 |
| 42* | 935 | 12:40 | 4:00 | 180 | 55 | 415 | 11:15 | 11:18 | 3 |
| 43 | 443 | 11:19 | 11:24 | 5 | | | | | |

* Cone froze.

TABLE VI

ARRANGED IN ORDER OF TEMPERATURE DEFORMATIONS

| Member | Temp. (°C) | Interval (min.) | Member | Temp. (°C) | Interval (min.) |
|---|---|---|---|---|---|
| 36 | 400 | 2 | 43 | 443 | 5 |
| 45 | 405 | 2 | 28 | 447 | 5 |
| 54 | 405 | 3 | 35 | 455 | 4 |
| 55 | 415 | 3 | 27 | 455 | 5 |
| 44 | 417 | 3 | 21 | 470 | 6 |
| 52 | 425 | 2 | 34 | 515 | 3 |
| 53 | 430 | 4 | 51 | 950 | |

This series showed no relation between cone deformation and viscosity.

**Study D** The fourth area studied was bound by members 17, 21, and 51. These members have the following compositions:

| Member | | | |
|---|---|---|---|
| 17 | CaO | $3.0B_2O_3$ | $0.8SiO_2$ |
| 21 | CaO | $19B_2O_3$ | $4SiO_2$ |
| 51 | CaO | $3.8B_2O_3$ | |

Members 21 and 51 having been used in previous studies were already prepared. Member 17 was held in fused state in a platinum dish at 1000°C for about two hours. Owing to scum forming on top of a clear glass this member was fused a second time.

TABLE VII

END MEMBERS 17, 21, 51; 4% INTERVALS

| Member | Temp. (°C) | Time "Started" | Time "Down" | Interval (min.) |
|---|---|---|---|---|
| 24 | 945 | Very fast about 30 sec. | | |
| 25* | 940 | 11:55 | 1:09 | 74 |
| 26 | 560 | 11:16 | 11:19 | 3 |
| 32* | 950 | 12:01 | 1:09 | 68 |
| 33 | 950 | Very fast about 30 sec. | | |
| 41 | 945 | 1:01 | 1:09 | 8 |

* Cones froze.

This series showed no relation between cone deformation and viscosity.

Figure 5 is an isothermal diagram showing the results of the cone deformation study in studies A, B, C, and D given above in detail. The diagram as a whole shows a general sloping or trend in deformation tem-

TABLE VIII

ARRANGED IN ORDER OF TEMPERATURE DEFORMATIONS

| Member | Temp. (°C) | Interval (min.) |
|---|---|---|
| 26 | 560 | 3 |
| 25 | 940 | 74 |
| 41 | 945 | 8 |
| 24 | 945 | ½ |
| 33 | 950 | ½ |
| 32 | 950 | 68 |

peratures toward the high $B_2O_3$ area. This sloping or trend is very abrupt or precipitous from member 16 down through 51 and 52. The members deforming at 950°C or higher had very low viscosity or deformed quite rapidly, suggesting the possible formation of a compound or compounds with definite melting points. In this study conducted at approximately 4% intervals there is no evidence of an isolated member having the lowest deformation temperature.

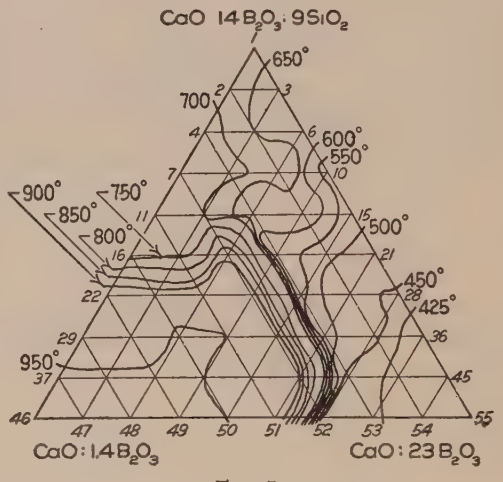



FIG. 5.

## Eutectics as an Enamel Base

Since there was no evidence of a deformation eutectic from the cone fusion study (Fig. 5) it was necessary to select from that study a member high in lime and silica which is isotropic (well vitrified with everything in solution). This member was to be blended with other eutectics in order to develop a solvent for an enamel.

The following members were heat-treated to quiet fusion and then air-quenched by pouring into a cast-iron ingot mold where they were allowed to cool. They were then examined microscopically to see if any crystalline material was present and how much glass was present.

(A) ($CaO$–$6.0B_2O_3$–$5.0SiO_2$) was fused in a fused silica crucible. This fused member showed a large amount of crystalline material with some glass matrix.

(B) ($CaO$–$5.0B_2O_3$–$6.0SiO_2$) was fused in a sillimanite crucible. This fused member also showed a considerable amount of crystalline material with some glass matrix.

(C) ($CaO$–$2.5B_2O_3$–$2.5SiO_2$) was fused in a fused silica crucible. This fused member showed a considerable amount of crystalline material with some glass matrix.

(D) ($CaO$–$1.33B_2O_3$–$1.66SiO_2$) was fused in a fused silica crucible. This fused member showed a rather large amount of crystalline material (more than C) with glass matrix.

Members 1 and 21 had been fused only once before while member 16 had been fused twice. These members were all fused again in a platinum dish.

Member 1 ($CaO$–$14B_2O_3$–$9SiO_2$): This fused member formed an opaque viscous glass with a small amount of crystalline material present.

Member 16 ($CaO$–$2.33B_2O_3$–$0.66SiO_2$): This fused member formed an opaque white glass on top with some clear glass below. Both were apparently true glasses with no evidence of crystalline material present.

Member 21 ($CaO$–$19B_2O_3$–$4SiO_2$): This fused member also formed an opaque white glass on top with some clear glass below very similar to member 16.

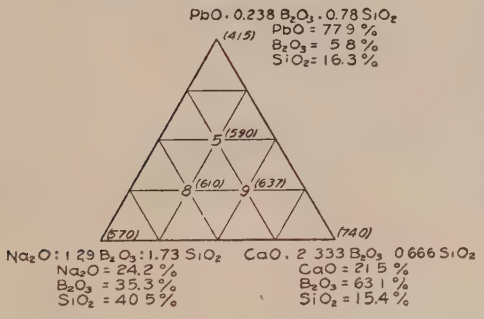



FIG. 6.

Inasmuch as $SiO_2$ could be added later it was decided to select member 16 as it was highest in lime. It had the following composition: $CaO$ 21.5%, $B_2O_3$ 63.1%, $SiO_2$ 15.4%.

Member 16 was selected as one end member of a triaxial study while the lead borosilicate eutectic ($PbO$ 0.238 $B_2O_3$ 0.78 $SiO_2$) developed by Lu[5] and the soda borosilicate eutectic ($Na_2O$ 1.29 $B_2O_3$ 1.73 $SiO_2$) also developed by Lu,[5] were used as the other end members of the triaxial. These are shown graphically in Fig. 6.

The three intermediate members 5, 8, and 9 were made up by blending the end members and a cone deformation study made of them. The results are shown in Fig. 6, the high lead member 5 giving the earliest deformation (590°C), the high soda member 8 being next in order of deforma-

[5] *Jour. Amer. Ceram. Soc.*, **9**, 29–54 (1926).

tion (610°C), while the high lime member 9 was the most refractory (740°C). This is what might be expected by mixing of end members with wide differences in degrees of deformation, that is, the intermediate members lie within the limits of the various end members. Members 5, 8, and 9 are, no doubt, mixtures and no evidence of deformation eutectic is seen.

In order to increase the refractoriness, durability, and acid resistance of these bases one molecule of $SiO_2$ was added to each member 5, 8, and 9. They were called 5A, 8A, and 9A, respectively. These members were made up on a 1000-g. raw batch basis and fritted in a high bauxite crucible. The members were held in the fused state until bubbling had ceased and a fairly clear glass could be drawn from the fusions. The high lead members

| Member 5 | (%) | | |
|---|---|---|---|
| PbO | 38.95 | | |
| $Na_2O$ | 6.05 | 0.48 PbO | 1.00 $SiO_2$ |
| CaO | 5.38 | 0.26 $Na_2O$ | 1.06 $B_2O_3$ |
| $B_2O_3$ | 27.51 | 0.26 CaO | |
| $SiO_2$ | 22.12 | | |

| Member 8A | (%) | | |
|---|---|---|---|
| PbO | 15.80 | | |
| $Na_2O$ | 9.75 | 0.23 PbO | 2.24 $SiO_2$ |
| CaO | 4.50 | .51 $Na_2O$ | 1.32 $B_2O_3$ |
| $B_2O_3$ | 28.50 | .26 CaO | |
| $SiO_2$ | 41.50 | | |

| Member 5A | (%) | | |
|---|---|---|---|
| PbO | 32.20 | | |
| $Na_2O$ | 4.85 | 0.48 PbO | 2.00 $SiO_2$ |
| CaO | 4.40 | .26 $Na_2O$ | 1.06 $B_2O_3$ |
| $B_2O_3$ | 22.40 | .26 CaO | |
| $SiO_2$ | 36.20 | | |

| Member 9 | (%) | | |
|---|---|---|---|
| PbO | 19.48 | | |
| $Na_2O$ | 6.05 | 0.23 PbO | 1.97 $SiO_2$ |
| CaO | 10.75 | .26 $Na_2O$ | 1.58 $B_2O_3$ |
| $B_2O_3$ | 41.83 | .51 CaO | |
| $SiO_2$ | 21.90 | | |

| Member 8 | (%) | | |
|---|---|---|---|
| PbO | 19.48 | | |
| $Na_2O$ | 12.10 | 0.23 PbO | 1.24 $SiO_2$ |
| CaO | 5.38 | .51 $Na_2O$ | 1.32 $B_2O_3$ |
| $B_2O_3$ | 34.88 | .26 CaO | |
| $SiO_2$ | 28.18 | | |

| Member 9A | (%) | | |
|---|---|---|---|
| PbO | 15.70 | | |
| $Na_2O$ | 4.95 | 0.23 PbO | 1.97 $SiO_2$ |
| CaO | 8.80 | .26 $Na_2O$ | 1.58 $B_2O_3$ |
| $B_2O_3$ | 34.20 | .51 CaO | |
| $SiO_2$ | 36.40 | | |

5 and 5A were made by first heating the crucible to a bright red heat, then adding the raw material with a scoop and finishing the fritting as rapidly as possible. The actual fritting usually required from one-half to three-quarters of an hour. The frits were quenched in water, dried over a hot plate, and dry ground in a porcelain ball mill to pass a 60-mesh screen.

About 300 g. of each member were then ground for 5 hours with 5% German Vallender clay and about 66% water. The mixtures were later "set up"[6] by adding 1% borax dissolved in hot water. The members used had the molecular composition and percentage shown above.

These members were tried both as ground coats and cover coats on cast-iron trials. The ground coat was sprayed on and showed very little prom-

[6] The term "set up" is used to indicate a material that on addition to the enamel prevents the grains of material from settling out.

ise, the enamel crawling considerably. When tried as a cover coat over a commercial ground coat and applied by the dry process, these members all showed considerable promise. The cover coats were dusted or dredged on using a 50-mesh screen.

The ground coat used was a black ground coat and had been previously tried out to satisfaction with some commercial cover coats. This ground coat had the following composition:

| Frit | | Mill addition | (%) |
|---|---|---|---|
| Borax | 266 | Clay (Fla. kaolin) | 6 |
| Flint | 164 | $MgCO_3$ | 1 |
| Feldspar | 145 | CoO | 2 |
| Soda ash | 36.5 | $MnO_2$ | 0.7 |
| $NaNO_3$ | 26.5 | $Fe_3O_4$ | 0.2 |
| Fluorspar | 35.0 | CuO | 0.1 |
| $MnO_2$ | 11.25 | Frit | 100.0 |
| $NiO_2$ | 6.5 | Applied at sp. gr. 1.52; fired | |
| CoO | 5.5 | 1450–1550°F | |

## Results of Dry-Process Cover-Coat Test on Black Ground Coat Given Above

They were fired at 1400°F and 1500°F.

Member 5

1400°F: Fair surface, no chipping, no opacity; a second coat gave some opacity.
1500°F: Splendid surface, a little opacity, good enamel; a second coat gave a little opacity and better covering properties.

Member 5A

1400°F: Second coat gave fair enamel, no chipping, no opacity, but rather rough surface.
1500°F: Much better surface than at 1400°, no chipping; second coat showed some opacity.

Member 8

1400°F: Fair enamel, some opacity, no chipping, but rather rough surface.
1500°F: Better surface than at 1400°F; second coat gave fair opacity, but chipped some.

Member 8A

1400°F: Fair enamel, no opacity, no chipping, surface a little rough.
1500°F: Good enamel, surface better than at 1400°F, no chipping; second coat showed a little opacity.

Member 9

1400°F: Poor enamel, some opacity, but poor surface and chipped badly.
1500°F: Surface better than at 1400°F, but enamel chipped badly.

Member 9A

Showed practically no possibility at these temperatures of 1400°F and 1500°F, as the enamel had not matured or vitrified.

These enamels were also used over a commercial ground coat that is being used for cast-iron ware as sinks, water fountains, etc., in the industry. The composition of the ground coat is not known, but it was fired to 1650°F and gives an idea of the behavior of enamels at a higher temperature.

**Results of Dry-Process Cover-Coat Test on Commercial Ground Coat Fired at 1650°F**

Member 5: Fine enamel, splendid surface, no chipping, some opacity.
Member 5A: Enamel chipped badly, otherwise good.
Member 8: Fine enamel, good surface, considerable opacity and no chipping.
Member 8A: Good surface, little opacity, but second coat chipped badly.
Members 9 and 9A: Good surface and fair opacity but enamel chipped badly.

In both studies the "A" series or high silica showed less opacity than the lower silica members, showing that silica was apparently going into solution in eutectic solvent. The increased chipping with the commercial ground coat is believed to be due in part by the thin coating of ground coat used, giving a poor bond between metal and cover coat.

## Action of Various Acids on Enamels

The relative action on a given enamel of different acids and of various strengths of the same acid has been the subject of considerable investigation.[7]

The following acid tests were made in this investigation, using 20% HCl solution:

**(1) Drop Test** One drop of HCl (20%) was placed on the surface of the enamel and allowed to stand for one minute. It was then rubbed off with a wet sponge and rubbed dry with a clean towel.

**(2) Surface Test** A surface approximately $^1/_2$ inch in diameter was walled in or surrounded with paraffin. One-half cc. of HCl (20%) was placed in this area and allowed to evaporate at room temperature (21°C) requiring about 10 hours.

**(3) Granulated Frit Test** Two grams of frit, finer than 60-mesh, were placed in a 400-cc. beaker and 200 cc. of HCl (20%) were added. The contents were stirred thoroughly and allowed to stand for twenty-four hours. The undissolved portion was then recovered on a Gooch crucible. Some of the members formed a gel which could not be filtered and for this reason this method was abandoned as unpractical.

The results of the acid tests were as follows:

| Drop Test, Member No. | 1400°F | 1500°F | 1650°F |
|---|---|---|---|
| 5 | Slightly etched | Slightly etched | Slightly etched |
| 5A | Less than 5 | Less than 5 | Less than 5 |
| 8 | Slightly etched | Slightly etched | Slightly etched |
| 8A | No etching | No etching | No etching |
| 9 | Slightly etched | Slightly etched | Slightly etched |
| 9A | x | x | No etching |

x is immature, not tested.

[7] See Bibliography, ref. 40 through 45.

| Surface Test, Member No. | 1400°F | 1500°F | 1650°F |
|---|---|---|---|
| 5 | Etched through to metal | Etched through to metal | Etched through to metal |
| 5A | " " " " | " " " " | " " " " |
| 8 | " " " " | " " " " | " " " " |
| 8A | Etched on surface | Etched on surface | Etched on surface |
| 9 | Etched through to metal | Etched through to metal | Etched through to metal |
| 9A | x | x | Etched on surface |

x is immature, not tested.

Member 5: Could not be filtered on Gooch crucible as a gel had formed
Member 5A: 56.85% soluble
Member 8: 69.00% "
Member 8A: 50.60% "
Member 9: Could not be filtered on Gooch crucible as gel had formed
Member 9A: 56.50% soluble

The different tests in general gave the same results. There was no doubt in each case of the high soda, 8A member, as being the most acid resistant, while 9A at 1650°F was next, and 5A was next. There was no evidence of increase in acid resistance by increase in firing temperature.

Inasmuch as member 8A looked to be most promising it was decided to work close to this member and still add more silica. One-half molecule of $SiO_2$ was added to 8A and this member called 8B. An intermediate member between 8A and 5A plus one-half molecule $SiO_2$ was made up called 85B. An intermediate member between 8A and 9A plus one-half molecule $SiO_2$ was made up and called 89B. Members 8B, 85B, and 89B were fused in high bauxite crucibles as explained above in fusions of members 5, 5A, etc. Four intermediate members X, Y, Z, and W were made up by blending 8B, 85B, and 89B as shown in Fig. 7.

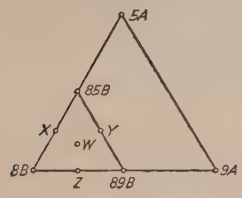


FIG. 7.

The percentage compositions and molecular compositions are as follows:

| Member 8B | (%) | | | Member X | (%) | | |
|---|---|---|---|---|---|---|---|
| PbO | 14.4 | | | PbO | 18.1 | | |
| $Na_2O$ | 9.0 | 0.23 PbO<br>.51 $Na_2O$<br>.26 CaO | 2.74 $SiO_2$<br>1.32 $B_2O_3$ | $Na_2O$ | 7.9 | 0.29 PbO<br>.45 $Na_2O$<br>.26 CaO | 2.68 $SiO_2$<br>1.26 $B_2O_3$ |
| CaO | 4.1 | | | CaO | 4.1 | | |
| $B_2O_3$ | 26.0 | | | $B_2O_3$ | 24.7 | | |
| $SiO_2$ | 46.5 | | | $SiO_2$ | 45.2 | | |
| | 100.0 | | | | 100.0 | | |

| Member 85B | (%) | | | Member Y | (%) | | |
|---|---|---|---|---|---|---|---|
| PbO | 21.8 | | | PbO | 18.1 | | |
| $Na_2O$ | 6.8 | 0.35 PbO<br>.39 $Na_2O$<br>.26 CaO | 2.62 $SiO_2$<br>1.19 $B_2O_3$ | $Na_2O$ | 6.8 | 0.29 PbO<br>.38 $Na_2O$<br>.32 CaO | 2.62 $SiO_2$<br>1.32 $B_2O_3$ |
| CaO | 4.1 | | | CaO | 5.0 | | |
| $B_2O_3$ | 23.4 | | | $B_2O_3$ | 26.0 | | |
| $SiO_2$ | 44.0 | | | $SiO_2$ | 44.1 | | |
| | 100.1 | | | | 100.0 | | |

| Member 89B | (%) | | |
|---|---|---|---|
| PbO | 14.4 | | |
| $Na_2O$ | 6.8 | 0.23 PbO | 2.61 $SiO_2$ |
| CaO | 6.0 | .39 $Na_2O$ | 1.45 $B_2O_3$ |
| $B_2O_3$ | 28.6 | .38 CaO | |
| $SiO_2$ | 44.2 | | |
| | 100.0 | | |

| Member Z | (%) | | |
|---|---|---|---|
| PbO | 14.4 | | |
| $Na_2O$ | 7.9 | 0.23 PbO | 2.68 $SiO_2$ |
| CaO | 5.0 | .45 $Na_2O$ | 1.39 $B_2O_3$ |
| $B_2O_3$ | 27.3 | .32 CaO | |
| $SiO_2$ | 45.4 | | |
| | 100.0 | | |

| Member W | (%) | | |
|---|---|---|---|
| PbO | 16.9 | | |
| $Na_2O$ | 7.6 | 0.27 PbO | 2.65 $SiO_2$ |
| CaO | 4.8 | .44 $Na_2O$ | 1.21 $B_2O_3$ |
| $B_2O_3$ | 26.0 | .29 CaO | |
| $SiO_2$ | 45.0 | | |
| | 100.3 | | |

These members were all used as cover coats (dry process) on the black ground coat. The results were as follows:

Member 8B, 1650°F: Fair surface, a little opacity, no chipping.
Member X, 1650°F: Good surface, a little opacity, small amount of chipping around edges.
Member 85B, 1650°F: Fair surface, a little opacity, small amount of chipping around edges.
Member Y, 1650°F: Good surface, practically no opacity, considerable chipping.
Member 89B, 1650°F: Fine surface, no opacity, small amount of chipping on edges.
Member Z, 1650°F: Good surface, a little opacity, small amount of chipping around edges.
Member W, 1650°F: Fine surface, a little opacity, small amount of chipping on edges.

The chipping was most pronounced in members Y and 89B or toward high lime content. The chipping appeared to be greater on trials with two coats, suggesting that increased thickness may have had something to do with chipping. This chipping occurred on trials principally after they had been subjected to acid test.

The results of the acid tests were as follows:

Drop test

Member 8B: No evidence of attack
" X: " " " "
" 85B: Slightly etched
" Y: " " more than 85B
" 89B: " " " " Y
" Z: Very slightly etched
" W: " " " like Z

Surface test

Member 8B: Slightly etched; good resistance
" X: Slightly etched; not as good as 8B
" 85B: Etched some; not as good as X
" Y: Etched badly
" 89B: Etched badly; poor resistance
" Z: Etched badly, but better than 89B
" W: Etched slightly; similar to X

The results of these tests pointed conclusively to member 8B, or high $Na_2O$ member as being most acid resistant with X and 85B, or high PbO member next in acid-resisting properties. The high lime, or 89B, appeared to be the least resistant.

## Water Solubility

A 10-gram sample was weighed and placed in a glass tumbler and 100 cc. of distilled water were added. The mixture was stirred thoroughly and allowed to stand for twenty-four hours. The mixture was again stirred thoroughly and filtered through porcelain filter tubes using a suction pump. The experiment was carried out at room temperature of 21°C. A blank was also run to test the purity of the water and the possible solubility of the glass tumbler in the water. The following results were obtained:

| Blank run | (Grams) |
|---|---|
| Wt. of Pt dish + residue | 41.529 |
| Wt. of Pt dish | 41.528 |
| Residue | .001 |

This represents the amount of glass dissolved in 25 cc. of water and any soluble salts present in the water itself and should be subtracted from the determined weight to get the actual amount of dissolved frit.

Table of Solubility of Frits in Water

| Member | Wt. sol. in 25 cc. $H_2O$ (Grams) | Wt. sol. in 100 cc. $H_2O$ | Per cent of original 10 g. sol. in 100 cc. $H_2O$ |
|---|---|---|---|
| 5 (high PbO) | 0.046 | 0.184 | 1.84 |
| 5A | .026 | .104 | 1.04 |
| 85B | .028 | .112 | 1.12 |
| 8 (high $Na_2O$) | .169 | .676 | 6.76 |
| 8A | .040 | .160 | 1.60 |
| 8B | .039 | .156 | 1.56 |
| 9 (high CaO) | .130 | .520 | 5.20 |
| 9A | .104 | .416 | 4.16 |
| 89B | .044 | .176 | 1.76 |

The high lead borosilicate was the least soluble, the high lime borosilicate next, and the high soda borosilicate was the most soluble.

On increase in $SiO_2$ by one molecular equivalent the solubility in water was decreased. This decrease in solubility was most marked in the high soda member or from members 8 to 8A. With the further addition of one-half molecular equivalent of $SiO_2$ to member 8A the solubility was decreased a very small amount, 0.04% showing that increase in $SiO_2$ over one equivalent has very little effect on its solubility in water for this particular high soda member.

Member 85B, which was a new fusion with a composition of one-half member 8A and one-half member 5A plus one-half molecule of $SiO_2$, had a percentage solubility between 5A and 8A. Member 89B, which was also

a new fusion with a composition of one-half member 8A and one-half member 9A plus one-half molecule of $SiO_2$, had a percentage solubility between 8A and 9A.

## Summary

After the examination, microscopically, of many members high in $SiO_2$ and CaO, member 16 (CaO 21.5%, $B_2O_3$ 63.1%, $SiO_2$ 15.4%) was chosen as the most practical member available as a means of introducing CaO into the enamel. This member is only a mixture and not a eutectic but it showed, on repeated fusion, complete solution of all constituents, and being high in lime and fairly high in $SiO_2$ was chosen as the most desirable member.

**(a) Brilliance and Smoothness of Surface Developed** — High lead members were best; high soda members were next; and high lime members were next.

The data obtained is classified as follows:

The lower fusion of the high lead members and their lower viscosity seemed to give these members a more brilliant and smoother surface.

The high soda members are close to high lead members in brilliance and smoothness of surface, and have a deformation point 20°C higher and a slightly greater viscosity.

The high lime members show very little promise, having a considerably higher deformation point (40°C) than the high soda member and a slightly greater viscosity. They were not matured or not enamels at temperatures of 1400 to 1500°F, which are the working temperatures employed.

Smoothness is a very essential property in an enamel coat so that no foreign material is likely to lodge or stick to the surface. This cleanliness of a smooth surface is bound to add to the life and service of an enamel.

**(b) Faults in Texture and Bond** — The tendency to chip was least in the high soda members and greatest in the high lime members. The high lead showed more tendency to chip than high soda members but less than high lime. The tendency to chip was all on the edges of the trial pieces.

The enamels showed no other faults such as blistering, fishscaling, crazing, etc.

**(c) Solubility in Water** — Since practically all enamel frits are quenched in water and since most enamels are applied to the metal in slip form or suspended in water, a knowledge of the solubility of the enamels in water was advantageous.

The high lead borosilicate member was found to be the least soluble, the high lime borosilicate next, and the high soda borosilicate was the most soluble.

**(d) Resistance to Acid Attack** The high soda members showed the greatest resistance to acid attack. The high lead members were next and high lime members the least resistant to acid attack.

This question of acid resistance is of importance in the manufacture of ware to be used in making of chemicals, explosives, and certain food products. Manufacturers of enameled ware to be used in cooking and for other purposes in which enamel will come in contact with dilute acids are also interested in this problem.

**(e) Effect of Additions of $SiO_2$ to Enamels** The enamel as fritted is complete, containing both solvent glass and refractory material, the only addition being a small amount of material such as clay and borax or other salt to "set up" or float the enamel in water in order that it may be applied by the wet process.

Therefore, the addition of $SiO_2$ or other refractory ingredients to the frit batch is an important consideration in this study and we find that $SiO_2$ additions change the properties of the base enamels as follows:

In the high lead members the brilliance of the surface was diminished, and at 1400°F the surface was not as smooth. The opacity is also slightly diminished. The tendency to chip is also increased at the higher firing temperature, 1650°F. The resistance to acid is increased considerably with additions of one molecule and with one and one-half molecules of silica.

The high soda members give about the same brilliancy in surface as the high lead members but opacity is decreased considerably with addition of one molecule of $SiO_2$. The tendency to chip is increased with addition of $SiO_2$ at the high firing temperature, 1650°F. With the addition of one and one-half molecules of $SiO_2$ some opacity is obtained but the surface is not as smooth as that of the members lower in $SiO_2$. The acid resistance is increased to a marked degree and there is no tendency to chipping when fired on the black ground coat.

The high lime members show little promise except when fired at high temperatures, 1650°F, and then their good qualities are overcome by a tendency to chip. The member 89B (formed by mixing the high lime member and the high soda member plus one-half molecule of $SiO_2$) showed a brilliant and smooth surface with fairly good acid-resistant qualities, but it still had a tendency to chip on the edges of the trials.

On increase in $SiO_2$ by one molecular equivalent the solubility in water was decreased. This decrease is much more pronounced in the high soda member, being from 6.76 to 1.60%. With further increase in $SiO_2$ by one-half molecular equivalent a very small decrease in solubility was noted in the high soda member from 1.60 to 1.56%.

On blending high soda with high lead and high lime members and adding

one-half molecule of $SiO_2$ the solubility approached that of the lowest end member.


## Acknowledgment

The author wishes to express deep appreciation to Prof. Arthur S. Watts of the Department of Ceramics who directed this investigation, to Dr. W. J. McCaughey, who advised in the microscopic work, to Prof. G. A. Bole and Prof. R. M. King of the Department of Ceramics who reviewed this paper. The author is also grateful to the D. A. Ebinger Sanitary Manufacturing Company of Columbus, Ohio, who furnished sandblasted cast-iron samples and coöperated splendidly in carrying out this work.


## Bibliography


1. H. F. Staley, *Trans. Amer. Ceram. Soc.*, **13,** 668–80 (1911).
2. J. W. Mellor, A. Latimer, and A. D. Holdcroft, *Trans. Ceram. Soc.* [Eng.], **9,** 129 (1909–10).
3. W. Mostowitsch, *Metallurgie*, **4,** 647–55 (1910).
4. Beck, Löwe, and Stegmüller, *Arb. kais. Gesundh.*, **33,** 203–49.
5. H. Eisenlohr, *Sprechsaal*, **43,** 389–92.
6. H. Pictorius, *ibid.*, **43,** 576–77.
7. Morey and Fenner, *Jour. Amer. Chem. Soc.*, **39,** 1173–1229.
8. B. A. Rice, *Jour. Amer. Ceram. Soc.*, **6,** 525–47 (1923).
9. G. W. Morey and N. L. Bowen, *Jour. Phys. Chem.*, **28,** 1167.
10. Jäger and Von Klooster, *Sprechsaal*, **52,** 257.
11. A. S. Watts, *Trans. Amer. Ceram. Soc.*, **18,** 632 (1916).
12. Rankin and Wright, *Amer. Jour. Sci.*, **39,** 1–79.
13. Hanna, *Trans. Amer. Ceram. Soc.*, **17,** 672 (1915).
14. Hobart M. Kraner, *Jour. Amer. Ceram. Soc.*, **9,** 319–23 (1926).
15. Kerl, "Handbuch der Thonwarenindustrie," p. 1401.
16. Rankin and Merwin, *Amer. Jour. Sci.*, **45,** 304.
17. A. S. Watts, *Trans. Amer. Ceram. Soc.*, **19,** 453 (1917).
18. Singer, "Die Keramic im Dienste von Industrie und Volkswirtschaft," p. 404.
19. Rankin and Merwin, *Amer. Jour. Sci.*, **55** (1918).
20. P. Eskola, *ibid.*, **4,** 331–75 (1922).
21. H. V. Thompson, *Trans. Ceram. Soc.* [Eng.], **18,** 510–11.
22. Guertler, *Z. anorg. allgem. Chem.*, **40,** 337.
23. F. de. Carli, *Atti accad. Lincei*, **5** [6], 41–47 (1927).
24. H. S. Von Klooster, *Z. anorg. allgem. Chem.*, **69,** 122.
25. V. Auger, *Compt. rend.*, **180,** 1602–1604 (1925); *Jour. Soc. Chem. Ind.*, **44B,** 498 (1925).
26. Brown and Partington, *Jour. Soc. Chem. Ind.*, **44,** 325–26T (1925).
27. Wallace, *Z. anorg. allgem. Chem.*, **35,** 187.
28. P. Lebedev, *ibid.*, **70,** 301.
29. P. Eskola, *Amer. Jour. Sci.*, [V] **4,** 331–75 (1922).
30. Ferguson and Merwin, *Amer. Jour. Sci.*, **48,** 109.
31. Rankin and Merwin, *Jour. Amer. Chem. Soc.*, **38,** 575.
32. C. T. Peddle, *Jour. Soc. Glass Tech.*, **4,** 1–107; **5,** 90.
33. O. von Keil and A. Dammann, *Stahl Eisen*, **45,** 890 (1925).
34. General Electric Co., Ltd., Brit. 14,532 (1924).
35. J. W. Greig, *Amer. Jour. Sci.*, [I] **13,** 73, 1–44; [II], **13,** 74. 133–54 (1927).
36. F. de Carli, *Atti accad. Lincei*, **5** [6], 41–47 (1927).
37. O. Glaser, *Centr. Mineral. Geol.*, Abt. App., 81096 (1926).
38. Kai Ching Lu, *Jour. Amer. Ceram. Soc.*, **9,** 29–54 (1926).
39. A. V. Bleininger and P. Teetor, *Trans. Amer. Ceram. Soc.*, **14,** 210 (1912).
40. R. D. Landrum, *ibid.*, **13,** 494–501 (1911).
41. H. F. Staley (discussion), *ibid.*, p. 499.
42. E. P. Poste, *ibid.*, **17,** 137–49, 762–66 (1915).
43. Leon J. Frost, *Jour. Amer. Ceram. Soc.*, **1,** 422 (1918).
44. E. P. Poste, *ibid.*, **2,** 32–43 (1919).
45. H. F. Staley, *ibid.*, **4,** 703, 717 (1921).

## Autobiography

I, Harold Ellis Simpson, was born in Columbus, Ohio, June 16, 1903. I began my secondary school education in the public schools of Columbus, Ohio, and continued until graduating from Columbus North High School in June, 1921. The next fall I entered Ohio State University in the College of Engineering. My first industrial experience was obtained at the Brunt Porcelain Company of Chaseland, Ohio, in the summer of 1923. In the summer of 1925, I obtained more industrial experience at the Peerless Brick Company, Columbus, Ohio. I received the degree of Bachelor of Ceramic Engineering in June, 1925. The following year I was appointed a coöperative fellow of the United States Bureau of Mines and Engineering Experiment Station of the Ohio State University, receiving the degree of Master of Science in June, 1926. The next year I was appointed a co-operative fellow of the United States Bureau of Standards and Engineering Experiment Station of the Ohio State University, where I continued my graduate work. The next two years were spent in graduate work at Ohio State University. In the summer of 1928 I obtained more industrial experience at Claycraft Mining and Brick Company, Taylor Station, Ohio. I received the degree of Doctor of Philosophy from Ohio State University in June, 1929.